

Mechanical Properties and Corrosion Characteristics of Thermally Aged Alloy 22

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MECHANICAL PROPERTIES AND CORROSION CHARACTERISTICS OF THERMALLY AGED ALLOY 22

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ABSTRACT

Alloy 22 (UNS N06022) is a candidate material for the external wall of the high level nuclear waste containers for the potential repository site at Yucca Mountain. In the mill-annealed (MA) condition, Alloy 22 is a single face centered cubic phase. When exposed to temperatures on the order of 600°C and above for times higher than 1 h, this alloy may develop secondary phases that reduce its mechanical toughness and corrosion resistance. The objective of this work was to age Alloy 22 at temperatures between 482°C and 760°C for times between 0.25 h and 6,000 h and to study the mechanical and corrosion performance of the resulting material. Aging was carried out using wrought specimens as well as gas tungsten arc welded (GTAW) specimens. Mechanical and corrosion testing was carried out using ASTM standards. Results show that the higher the aging temperature and the longer the aging time, the lower the impact toughness of the aged material and the lower its corrosion resistance. However, extrapolating both mechanical and corrosion laboratory data predicts that Alloy 22 will remain corrosion resistant and mechanically robust for the projected lifetime of the waste container.

Keywords: nuclear waste container, N06022, aging, mechanical properties, corrosion resistance.

INTRODUCTION

Alloy 22 (UNS N06022) is a nickel-based alloy, which contains approximately 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe). Alloy 22 has excellent resistance to pitting corrosion, crevice corrosion and stress corrosion cracking in halide containing environments.¹⁻¹¹ Consequently, Alloy 22 is a candidate material to fabricate the external layer of the high level nuclear waste containers for the potential repository site in Yucca Mountain, Nevada.¹²⁻¹³

Due to the heat generated by the radioactive decay of the waste, the containers might experience temperatures as high as 160°C during their first 1000 years of emplacement. The lifetime design of the containers is 10,000 years. Previous studies have shown that the mechanical and corrosion properties of Alloy 22 did not change when it was aged for up to 40,000 h at 427°C.^{4,6} However, it is known that precipitation of detrimental second phases occurs when Alloy 22 is aged at temperatures above 600°C.¹³⁻¹⁹ The precipitation of these secondary phases that are formed at temperatures approximately 600°C and higher affect the corrosion resistance in aggressive acidic solutions and the mechanical properties of wrought and welded Alloy 22.¹³⁻²⁴

The purpose of this work was to study the effect of aging time and aging temperature on the mechanical properties and corrosion behavior of Alloy 22 both wrought and welded.

EXPERIMENTAL TECHNIQUE

Aging studies and posterior mechanical and corrosion testing were carried out using wrought and welded Alloy 22 (N06022). (1) Wrought Material: For mechanical properties or Charpy impact test the samples were machined from 0.5-inch (12.7 mm) thick plate. The testing conditions of the notched samples were according to ASTM E 23.²⁵ Most of these tests were carried out using Heat 2277-6-3171 (Table 1). Samples were aged for times between 0.5 and 6,000 h at 593°C, 649°C, 704°C and 760°C. For the aging times of 2,000 and 16,000 h Heats 2277-3-3223 and 2277-0-3195 were used. Heat 2277-7-3173 was used for the aging temperatures of 260°C, 343°C and 427°C.⁶ For the Charpy impact energy testing, the samples were aged in air using an approximate shape and later machined to the final testing shape after aging. For the corrosion studies, the coupons were prepared from 0.25-inch (~6 mm) thick plate Heat 2277-6-3181 (Table 1) for the temperature range between 482°C and 760°C and from 0.5-inch thick plate of Heat 2277-7-3173 for the temperature range between 260°C and 427°C.⁶ (2) Welded Material: For the mechanical properties, coupons were prepared from 0.5-inch thick plate. The base metal was Heat 2277-9-3201 and the weld wire was from Heat 2277-8-3281 (Table 1). Gas Tungsten Arc Welding (GTAW) was carried in an argon atmosphere. The weld seam consisted on a single V and contained 9 passes. For the corrosion studies of welded material, two 0.125-inch (~3 mm) thick sheets of Alloy 22 Heat 2277-9-3237 (Table 1) were welded using Alloy 22 filler metal wire 0.125-inch diameter Heat 2277-8-3277 (Table 1). After welding the plates were sliced in strips approximately 0.5-inch wide. Each strip contained a weld seam in the center. The samples were aged for 0.25 h, 0.5 h, 1 h, 3 h, 6 h, 10 h, 30 h, 60 h, 100 h, 300 h, 600 h, 1000 h, 3,000 h and 6,000 h at 900°F (482°C), 1000°F (538°C), 1100°F (593°C), 1200°F (649°C), 1300°F (704°C) and 1400°F (760°C). Aging was performed in air, and afterwards, the samples were rapid air-cooled. The coupons for immersion testing contained by length approximately 1/3 of weld material and 2/3 of base material (1/3 at each side of the weld). Before testing the samples were cleaned by vapor blasting. Changes in the corrosion resistance were measured using standard immersion tests such as a boiling aqueous solution of 50% sulfuric acid (H₂SO₄) + 42 g/l of ferric sulfate (Fe₂(SO₄)₃) and boiling 2.5% hydrochloric acid (HCl). The first test solution is also called the Streicher test or ASTM G 28 A.²⁵ This electrolyte boils at 120°C and is highly oxidizing. The second test solution is highly reducing, was carried out according to ASTM G 31 and it boils at approximately 101°C.²⁵ The ASTM G 28 A test was carried out for 24 h and the boiling HCl test was carried out for a total time of 96 h (the electrolyte solution was changed every 24 h). In these two tests, the solutions were open to the atmosphere through a condenser and a scrubber. Since the solutions were boiling, it is assumed that the amount of dissolved oxygen was insignificant.

RESULTS AND DISCUSSION

Mechanical Testing (Impact Energy)

The Charpy or impact energy test measures the toughness of a material. That is, the higher the impact (Charpy) energy, the higher both the strength and the elongation of the material before rupture. Alloy 22 in the mill-annealed condition absorbs the maximum energy of 264 ft.lb (358 Joule) from the Charpy testing pendulum and does not break, only bends. However, if this alloy is aged at high temperatures, its

mechanical toughness decreases. Figure 1 shows the impact energy for Alloy 22 as a function of aging temperature and aging time. The toughness for the MA wrought material was approximately 264 ft.lb and an aging time of approximately 10 h is required at 760°C for Alloy 22 to start its mechanical degradation. The lower the temperature, the higher this threshold time. For aging temperatures of 427°C and below, aging times as high as 40,000 h did not cause a change in the impact energy.⁶ Figure 2 shows a similar graph for the impact energy as a function of aging temperature and aging time for GTAW Alloy 22 coupons. For the as-welded coupons, the impact energy was approximately 160 ft.lb, that is, the impact toughness of a GTAW microstructure was approximately 60% of the impact toughness of a wrought structure (Figure 1). Figure 2 shows that GTAW Alloy 22 also suffered higher toughness loss for higher aging temperatures and longer aging times. Moreover, for the welded coupons (Figure 2), the degradation of the mechanical properties at each temperature seemed to start at lower threshold times than for wrought coupons (Figure 1). It was shown before that the impact energy loss by the aged material correlated well with the amount of tetrahedrally close packed (PCP) phases present in the aged microstructure.²¹ Figure 3 shows the time that is needed at each aging temperature for the aged microstructure (wrought and GTAW) to reach a toughness of approximately 60% of the un-aged value. That is, Figure 3 shows the time needed for the aged coupons to reach a toughness of 150 ft.lb for the wrought microstructure (Figure 1) and 100 ft.lb for the GTAW microstructure (Figure 2). Figure 3 shows that, even though, a GTAW microstructure suffered toughness loss at shorter time than the wrought microstructure, the degradation rate of both microstructures was the same. If the slopes of both curves in Figure 3 are equated to $-Q_{ap}/R$, Q_{ap} is the apparent activation energy for the aging process in Alloy 22 and R is the gas constant. Calculations show that this apparent activation energy, as determined by Charpy impact energy mechanical testing, was 228 kJ/mol for wrought material and 235 kJ/mol for GTAW material. Figure 3 also shows that both wrought and welded Alloy 22 will retain at least 60% of its initial toughness value even if aged at 350°C for times as long as 10,000 years.

Immersion Corrosion Testing

Figures 4 and 5 show the corrosion rate of wrought and GTAW Alloy 22 in ASTM G 28A solution for seven aging temperatures and thirteen different aging times, respectively. The corrosion rate of aged Alloy 22 in this oxidizing solution (G 28A) increased gradually as the aging time and the aging temperature increased (for $T \geq 538^\circ\text{C}$). For samples aged at 482°C the corrosion rate remained the same, even after aging for 10,000 h (Figure 4). Observation of the tested coupons in the ASTM G 28 A solution showed preferential corrosion at the grain boundaries. At higher aging times deeper grain boundary attack was observed, and in certain testing conditions some grains fell away because they became completely detached from the samples.

Figures 6 and 7 show the corrosion rate of wrought and GTAW Alloy 22 in boiling 2.5% HCl solution, respectively. For both types of coupons, the corrosion rate increased approximately three times after a certain threshold aging time at each temperature. The higher the temperature the lower the threshold time. Figure 6 shows that for the wrought coupons, the corrosion rate decreased slightly with the aging time. This behavior seems to suggest that a small amount of aging would be beneficial for corrosion resistance. For the higher aging temperatures (760, 704 and 649°C), the corrosion rate seemed to reach a plateau for an intermediate aging time. This behavior is more noticeable for the GTAW coupons (Figure 7). For both types of samples aged at 482°C the corrosion rate remained the same, even after aging for 3,000 h. Observation of the tested coupons in boiling 2.5% HCl solution showed preferential intergranular attack which became deeper and wider as the aging time increased. At aging times of 1000 h and higher, preferential corrosion attack at twins inside the grains was observed.

Figures 8 and 9 show the effect of welding on the corrosion rate of Alloy 22. Most of the corrosion rates of wrought Alloy 22 were published before.^{13,21,22} Figure 8 shows the corrosion rate in ASTM G 28 A for wrought and as-welded coupons at two aging temperatures (760°C and 538°C) as a function of aging time. For all aging times, the corrosion rate of welded coupons was always higher than the corrosion rate of wrought coupons. For example, at the aging temperature of 760°C and at the aging time of 10 h, the corrosion rate of the welded coupons was approximately two times the corrosion rate of the wrought coupons. Figure 9 shows the corrosion rate in boiling 2.5% HCl solution for wrought and as-welded coupons at two aging temperatures (760°C and 538°C) as a function of aging time. For all aging times, the corrosion rate of welded coupons was always higher than the corrosion rate of wrought coupons. For the shorter aging times (up to 3-6 h) the corrosion rate of the welded coupons was approximately three times the corrosion rate of the wrought coupons; however, for aging times of 6 h and longer, the difference in the corrosion rate was smaller.

Figure 10 shows the time necessary at each aging temperature for Alloy 22 to reach a corrosion rate of 80 mpy (~ 2 mm/year) in ASTM G 28 A, both for wrought and welded materials (from Figures 4 and 5). Figure 10 shows that at each aging temperature, a shorter aging time is required for the welded material to reach the threshold corrosion rate of 80 mpy. This threshold value is generally the maximum allowed value for in-plant quality control. Figure 10 shows that the Arrhenius slopes for both materials are the same, that is, the degradation of the welded material started earlier than the degradation for the wrought material; however, the degradation rate was the same. If the slopes of both curves in Figure 10 are equated to $-Q_{ap}/R$, Q_{ap} is the apparent activation energy for the aging process in Alloy 22 and R is the gas constant. Calculations show that this apparent activation energy, as determined by corrosion testing in oxidizing conditions (ASTM G 28 A) was 261 kJ/mol for wrought material and 262 kJ/mol for GTAW material. A similar plot for corrosion in boiling 2.5% HCl (reducing conditions) showed $Q_{ap} = 244$ kJ/mol for wrought material and $Q_{ap} = 306$ kJ/mol for GTAW material. For the 2.5% HCl solution, the curves for both materials were not parallel as in the case of the ASTM G 28 A solution (Figure 10). Assuming that the aging mechanism remains the same at the lower temperatures, Figure 10 shows that if the Arrhenius relationship is extrapolated to aging temperatures of 300°C, aging times higher than 10,000 years would be necessary for Alloy 22 to show a degradation corresponding to a corrosion rate of 80 mpy.

CONCLUSIONS

- (1) The impact energy (toughness) of Alloy 22 in the MA wrought condition was 264 ft.lb and of the GTAW condition was 160 ft.lb.
- (2) Aging at temperatures in the range 593°C to 760°C caused a decrease in the toughness of both wrought and GTAW Alloy 22. The higher the aging temperature and the higher the aging time the larger the toughness loss.
- (3) Extrapolating mechanical toughness laboratory data suggest that Alloy 22 will retain at least 60% of its toughness even after aging it for 10,000 years at 350°C.
- (4) When wrought and welded Alloy 22 coupons were aged at temperatures between 538°C and 760°C, the corrosion rate in oxidizing (ASTM G 28 A) and reducing (boiling 2.5% HCl) solu-

tions increased both with the aging temperature and aging time.

- (5) For the same aging temperature and aging time, the corrosion rate of GTAW Alloy 22 was higher than the corrosion rate of wrought material.
- (6) The corrosion degradation rate of Alloy 22 due to high temperature aging was the same for wrought and GTAW materials.

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TABLE 1
CHEMICAL COMPOSITION OF SOME STUDIED ALLOY 22 HEATS (WT%)

Element	2277-6- 3181	2277-8- 3281	2277-6- 3171	2277-9- 3237	2277-8- 3277
C	0.004	0.006	0.002	0.0047	0.0066
Co	1.11	1.10	0.70	0.9	1.1
Cr	21.59	21.58	21.97	21.26	21.58
Fe	3.9	4.17	4.42	3.97	4.17
Mn	0.28	0.25	0.23	0.25	0.25
Mo	13.64	13.29	13.31	13.15	13.29
Ni	~56.3	~55.5	~56.25	~57.4	~56.3
P	0.013	NA	NA	0.01	0.005
S	<0.001	NA	NA	0.003	0.0031
V	0.17	0.18	0.15	0.21	0.18
W	3.03	3.18	2.86	2.90	3.18

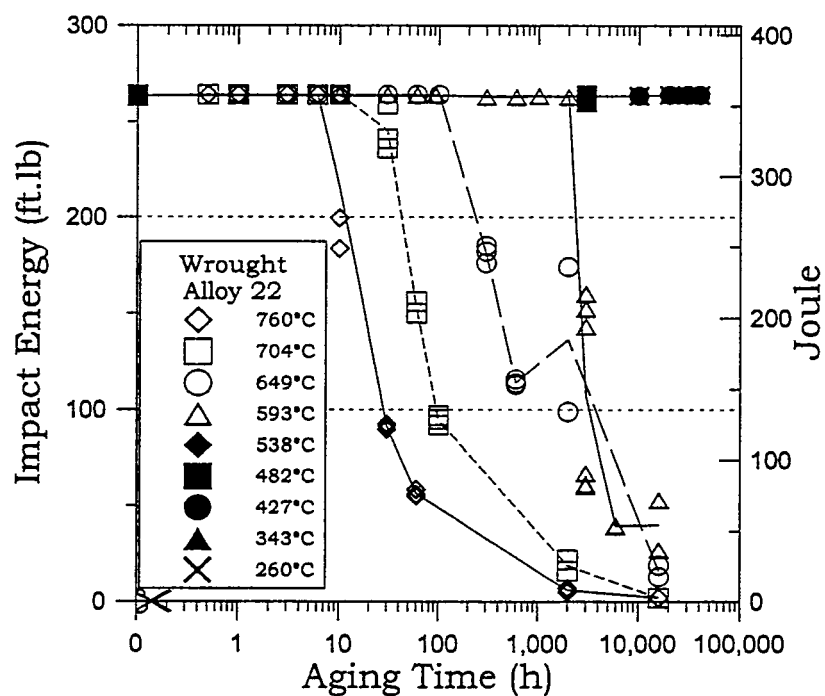


FIGURE 1: Impact energy for wrought Alloy 22 as a function of aging temperature and aging time.

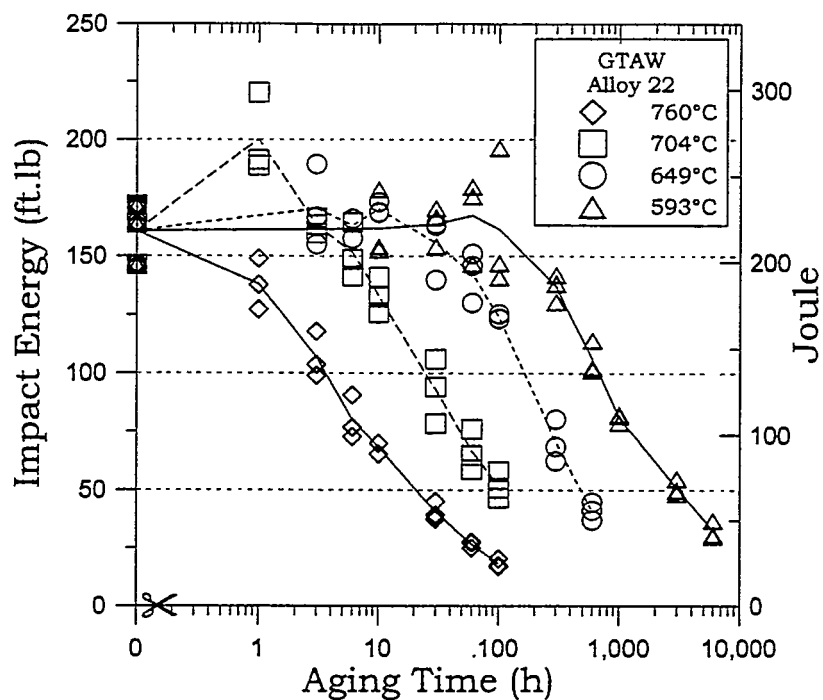


FIGURE 2: Impact energy for GTAW Alloy 22 as a function of aging temperature and aging time.

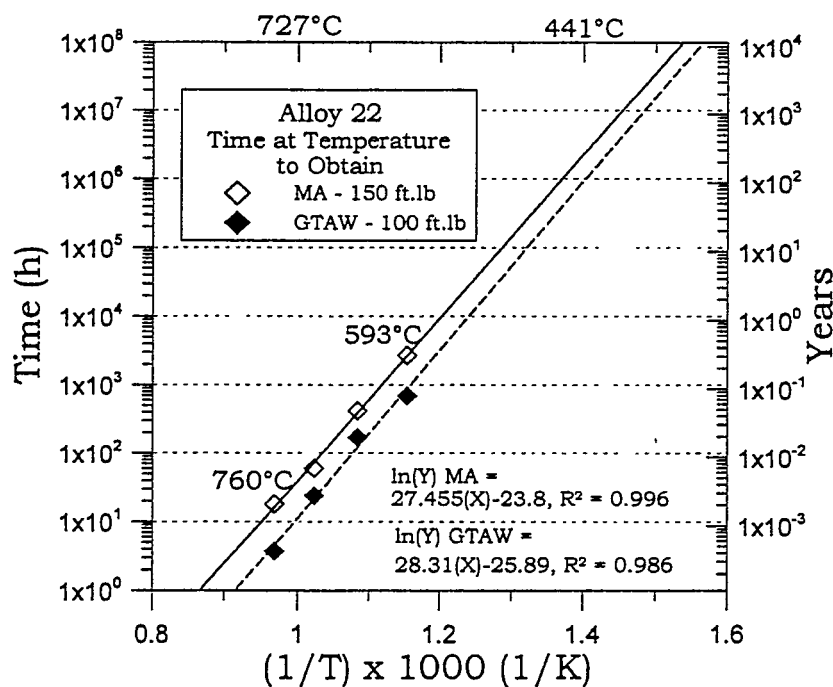


FIGURE 3: Arrhenius extrapolation based in the time needed at each temperature to reach an impact energy approximately 60% of its initial value.

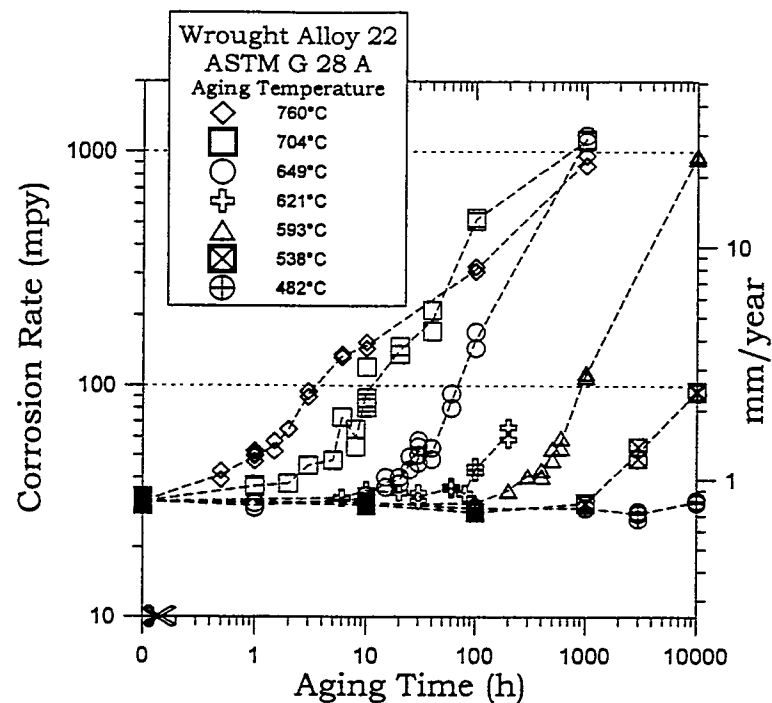


FIGURE 4: Corrosion rate of aged wrought Alloy 22 in ASTM G 28 A.

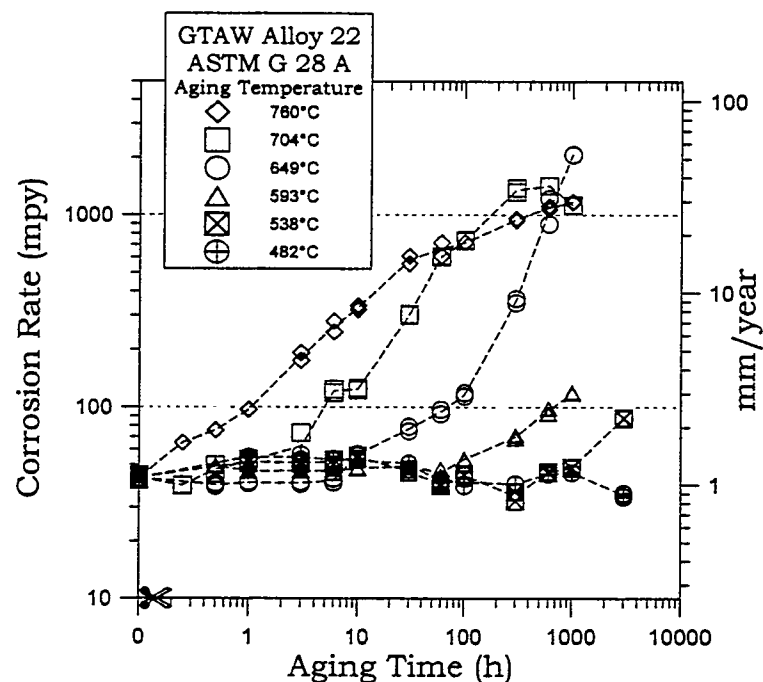


FIGURE 5: Corrosion rate of aged GTAW Alloy 22 in ASTM G 28 A.

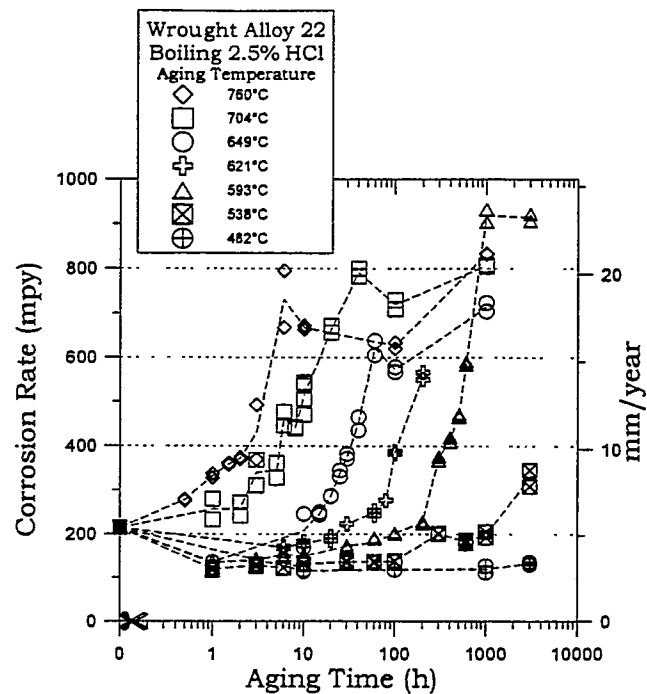


FIGURE 6: Corrosion rate of aged wrought Alloy 22 in boiling 2.5% HCl.

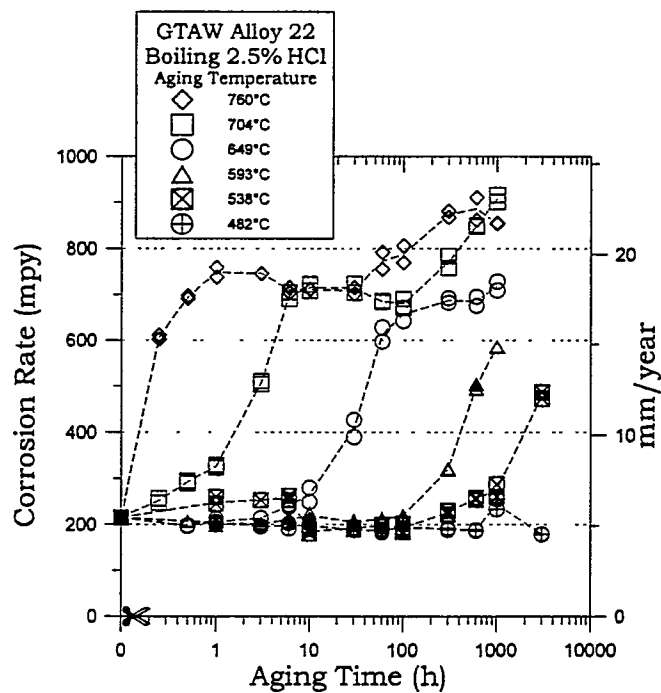


FIGURE 7: Corrosion rate of aged GTAW Alloy 22 in boiling 2.5% HCl.

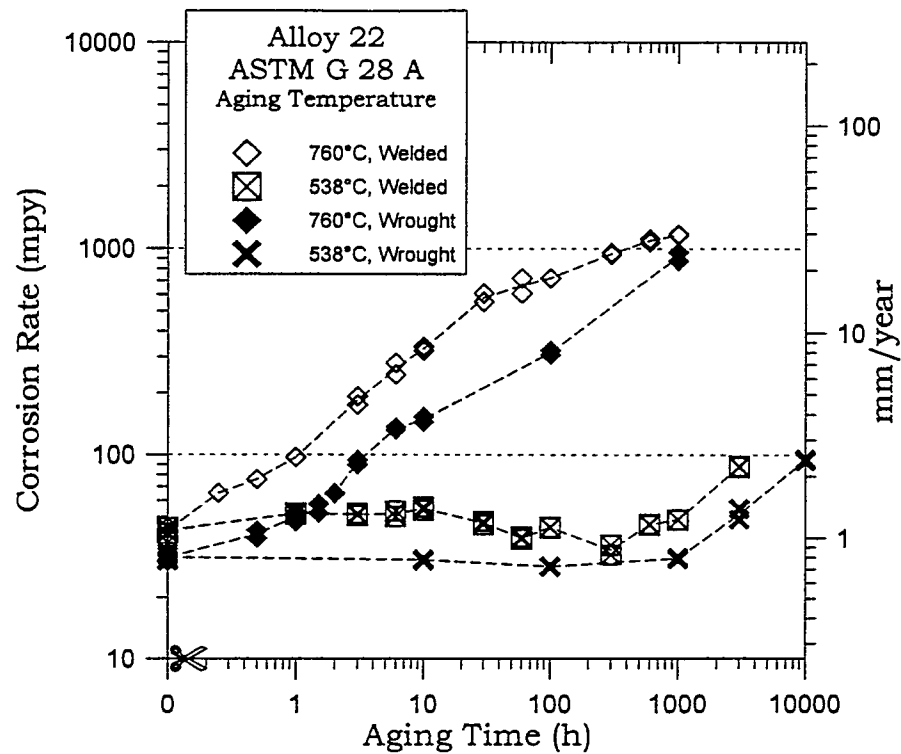


FIGURE 8: Corrosion rate in G 28 A solution for wrought and GTAW Alloy 22.

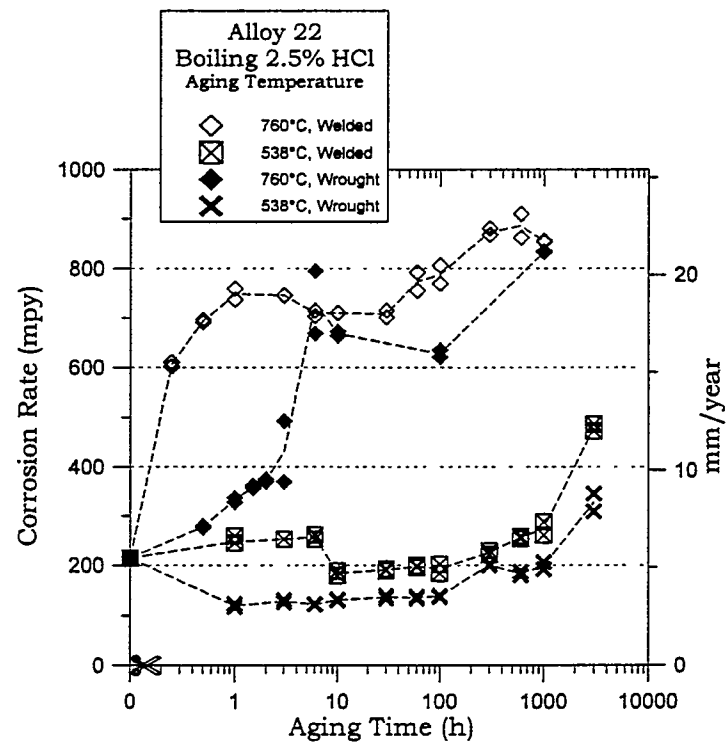


FIGURE 9: Corrosion rate in boiling 2.5% HCl solution for wrought and GTAW Alloy 22.

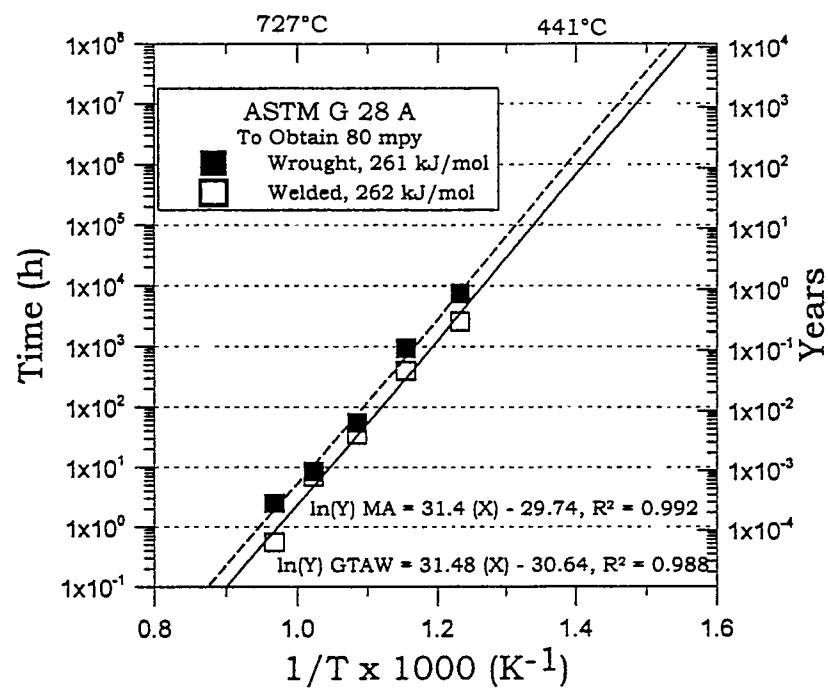


FIGURE 10: Arrhenius extrapolation for the corrosion behavior of wrought and GTAW Alloy 22.